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THE CHARACTERIZATION OF CARBON-14 CONTAINING PARTICULATE MATERIAL FROM THE GAS ANNULUS SYSTEMS OF PICKERING NGS 'A' UNITS 1 AND 2

Report No 86-73-K

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ABSTRACT

Microgram quantities of particulate material in a variety of samples from the gas annulus systems of Pickering Units 1 and 2 have been characterized with respect to particle size and morphology and chemical and radiochemical composition. The analytical techniques used include optical and electron microscopy, microgravimetry, autoradiography, γ-ray, x-ray and Auger electron spectrometry and liquid scintillation counting. The material, which has been observed as a black dust during the Pickering retubing operations, consists of ultrafine particles generally less than 10 μm in diameter exhibiting a variety of morphologies. Its chemical composition is variable but carbon, oxygen and iron are always the major constituents while small amounts of nitrogen are also usually present. The iron, which occurs mainly as Fe_2O_3 with small amounts of Fe_3O_4, stems from steel corrosion products while the carbon appears to be present as a polymeric, soot-like, material possibly containing small amounts of paracyanogen or similar compounds. The average carbon-14 specific activity of the material is estimated to be 0.17 ± 0.06 Ci/g of carbon, a value equivalent to a carbon-14 to carbon-12 ratio of about 4%. There is some γ-activity, mainly due to Co-60, detectable in the material but it is typically at least one thousand times lower than the carbon-14 activity.

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EXECUTIVE SUMMARY

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The use of nitrogen gas to fill the annular space between the pressure and calandria tubes in the Pickering NGS 'A' reactors has led to the production of substantial quantities of carbon-14, a long-lived (half life = 5730 years) beta-active isotope of carbon. The carbon-14 is produced when a nitrogen atom absorbs a neutron and releases a proton, a nuclear process also occurring naturally in the earth's upper atmosphere.

The fate of the carbon-14 produced in Hydro's reactors, and in particular its distribution and state of chemical combination in the gas annulus system, became a matter of concern following the discovery of a mysterious black dust on reactor components removed during the retubing of Pickering Units 1 and 2. The dust was easily dispersed into the reactor vaults and was subsequently found to have caused extensive radioactive contamination of exposed surfaces.

In March 1985 the contamination problem became so severe that retubing operations were suspended and only restarted after the implementation of new procedures designed to contain the dust and/or limit the exposure of personnel to it. At the same time work began at Chemical Research to characterize the black dust.

In the period from March 1985 to March 1986 seven different types of carbon-14 containing samples, including airborne particulate filters and smears from contaminated surfaces, were investigated by a variety of analytical techniques and are discussed in detail in this report.

It has been determined that the dust is not pure carbon-14, as first suspected, but a mixture of several components most of which are nonradioactive and act as carriers for the carbon-14.

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It is now believed that the carbon-14 produced in the nitrogen annulus gas system becomes attached to reactor surfaces, either directly or after reacting with other species, to form active deposits. The heaviest carbon-14 deposits found to date have been on the stainless-steel end-fitting bodies close to the bearing sleeves.

The adherence of the oxide scale formed on a gas annulus system surface is crucial to the mobilization and dispersion of a carbon-14 containing deposit. It appears, for example, that zirconium alloys do not form breakaway oxides and as a consequence zirconium is rarely associated with mobile carbon-14. By comparison, ferric oxide (Fe_2O_3) and magnetite (Fe_3O_4) particles, stemming from the corrosion of steel surfaces, are frequently associated with the carbon-14 and generally constitute a major component of the black dust.

Inactive carbon particles, possibly formed by the erosion of carbon vane pumps, are also major carriers of the carbon-14. Other species such as calcium, silicon, copper and zinc containing compounds have also been found in small amounts in the dust. All of these inactive species serve as inert diluents to the carbon-14 and lower its specific activity in the dust. In fact the carbon-14 has been found to constitute no more than 5% by weight of the black dust. Its activity is, none-the-less, at least one thousand times higher than any other radioactive species, e.g. cobalt-60, found in the dust.

Only limited progress has been made towards an identification of the chemical state of the carbon-14 in the dust from a Pickering gas annulus system. In this respect, at least, much of the mystery surrounding the material remains. The chemical properties of the dust investigated so far show that it is highly inert and quite insoluble in most common inorganic or organic solvents.

A consideration of the compounds identified by workers in the high energy discharge, sputtering or radiolysis of carbon/nitrogen systems shows that any carbon-14 species formed in a nitrogen gas annulus system should be akin to the polymer paracyanogen. The active species could then be represented by the formula $(^{14}CN)_n$. It is noteworthy that nitrogen has been found in the black dust at a concentration comparable to that of carbon-14.

The known properties of paracyanogen, such as its resistance to chemical attack and remarkable thermal stability, fit well with the behaviour of the beta-active species found in the Pickering

dust. However, it is stressed that the existence of paracyanogen-like compounds in the black dust remains a matter of conjecture and more investigations are required to confirm their presence.

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To Mr. F.J. Kee
Director of Research

THE CHARACTERIZATION OF CARBON-14 CONTAINING PARTICULATE MATERIAL FROM THE GAS ANNULUS SYSTEMS OF PICKERING NGS 'A' UNITS 1 AND 2

In the twelve and a half years of operation of the Pickering Unit 1 and 2 reactors nitrogen gas at atmospheric pressure was used to fill the annular space between the pressure and calandria tubes. The gas annulus system of a CANDU reactor serves to provide thermal insulation between the primary heat transport system and the moderator while dew point measurements of the annulus gas offer a convenient method for the detection of pressure tube leaks.

The exposure of nitrogen gas to an in-core flux of 8×10^{13} neutrons cm^{-2} s^{-1} results in the formation of carbon-14, via the $^{14}N(n,p)^{14}C$ reaction, at a rate of about 40 grams per unit per year/1/.

The fate of the carbon-14 produced in a gas annulus system remains largely unknown. Although the entire gas annulus systems of Pickering Units 1 and 2 were purged frequently, less than 10% of the expected inventory of carbon-14 has been found in the integrated gaseous emissions/2/. Consequently, over the operating lifetime of Units 1 and 2, it is expected that about 400 g of solid state carbon-14 has accumulated in each reactor.

The retubing of Pickering Units 1 and 2, which commenced in February 1985, has resulted in the release of some carbon-14 particulate material to the reactor vaults and has made CANDU produced carbon-14 the subject of extensive investigations. To date interest has focussed on the following topics:

(i) The distribution and ultimate state of chemical combination of carbon-14 in the gas annulus system/3,4/.

(ii) The release of carbon-14 during retubing operations/5,6/.

(iii) The behaviour of carbon-14 particulate in the human body following inhalation or ingestion/7/.

(iv) Carbon-14 decontamination and waste disposal/8/.

This report documents the results of analytical investigations carried out at Chemical Research during the period from March 1985 to March 1986. These investigations were designed to characterize carbon-14 containing particulate material from Pickering Units 1 and 2 with respect to several fundamental properties namely, particle size and morphology, specific activity and elemental composition. Some preliminary data of this type were previously reported/4,5,6/.

1.0 ANALYTICAL PROCEDURES

A wide variety of samples containing particulate carbon-14 have been submitted to Chemical Research for characterization. Because of difficulties in sample collection very small amounts of material, generally less than 1 mg, containing relatively low activities of carbon-14, 1 mCi or less, have been available from each sample for analysis. The samples have consisted mainly of carbon-14 containing material deposited onto substrates such as cellulose acetate or nitrate papers, polyester or silver membrane filters or quartz or glass wool swabs. In spite of this diversity of sample types a universal analytical procedure has been developed which is adaptable to any radioactive particulate sample with only minor modifications occasionally required in the initial stages of sample handling. This universal procedure evolved out of work on many samples over a period of almost one year; consequently samples received during the early stages of development work were subjected to only some parts of the procedure.

1.1 The Determination of Particle Size and Morphology

Optical microscopy was used to determine the size and morphology of particles down to approximately 1 μm in carbon-14 containing samples. Polyester membranes (Nuclepore filters) or glass plates (Andersen cascade impactor plates) were the only sample substrates suitable for direct particle size measurements by microscopy because of the limited depth of field available at the high magnifications required for small particle observation.

Samples submitted with particulate material deposited on substrates such as paper or glass wool required pretreatment to transfer material to a substrate such as polyester membrane. The pretreatment usually consisted of placing the sample in

water with sufficient agitation to resuspend some of the deposit followed by filtration through a 0.1 μm Nuclepore filter. Unfortunately glass or cellulose fibers tended to be put into suspension by this procedure, a problem which was overcome by prefiltration of the suspension through a 20 μm nylon sieve or a 12 μm Nuclepore filter.

Sub-micron carbon-14 containing particulate material was observed using conventional scanning electron microscopy or the secondary electron imaging capability of a scanning Auger Microprobe. Micrographs showing particles down to approximately 0.1 μm were produced by this technique. Indium foil (see Section 1.2) was used to mount particulate material for electron beam imaging in order to provide an electrically conducting substrate.

1.2 The Determination of Carbon-14 and Gamma Emitting Radionuclide Specific Activities

The specific activity of a sample expresses the amount of a radioactive species present in a given weight of sample material and is equivalent to a unit of concentration. Its evaluation therefore implies the measurement of a sample activity along with the corresponding sample weight. Because the samples submitted to Chemical Research for carbon-14 measurements generally consisted of only microgram amounts of active material deposited on substrates weighing in excess of a milligram the determination of the true sample weight was not a trivial problem. In some cases samples such as airborne particulate filters showed no visible deposit, except under high magnification in a microscope, but produced in excess of 10 000 cpm on a Geiger counter held a few centimetres away. Only occasionally did samples have enough active deposit for it to be transferred to a weighing boat.

The autoradiographic procedure reported in Reference 4 provided carbon-14 specific activities on some of the first samples investigated at Research but was imprecise and relied on several assumptions concerning the nature of the active material. The acquisition of a microbalance, with a sensitivity of 0.1 μg, has led to the development of specific activity measurement procedures which have been used successfully on as little as 1 μg of carbon-14 containing particulate.

The new procedure relies on the ability of indium, a highly malleable metal, to pick up microgram quantities of particulate material when lightly pressed against it. In detail, indium, approximately 1 mm thick, was cut into small squares, approximately 25 mm^2 in area, and weighed to ±0.1 μg on a Cahn Model 29 microbalance. A tared indium square was then pressed against

the sample under investigation, checked with a Geiger counter to ensure that active material had been picked up, and reweighed.

It was considered desirable to determine the specific activity of samples with respect to gamma emitting radionuclides as well as the pure beta emitter carbon-14. Consequently indium foils with active deposits were subjected to gamma spectrometric analysis in calibrated geometries using a hyperpure or a lithium drifted germanium detector.

Because all of the samples investigated in this study contained far more carbon-14 activity than gross gamma activity, a reasonable estimate (to within ±20%) of the amount of carbon-14 on an indium foil could be obtained by gross beta measurements in calibrated geometries using a Geiger counter/5/. Theoretical considerations show that such a Geiger counter measurement actually provides a lower limit to the true carbon-14 activity on a foil due to the neglect of self-absorption by large particles or thick deposit/4/. For this reason, when all other measurements had been completed on the deposited material, the indium foil was burnt in a Packard Tri-Carb Model 306 sample oxidizer and the absorption-corrected carbon-14 activity of the deposit determined by liquid scintillation counting.

1.3 The Determination of Elemental Composition

A quantitative determination of all the major elements in the carbon-14 containing samples, while certainly desirable, was considered to be unattainable for the microgram amounts of particulate material usually submitted for analysis. An additional constraint on the complete elemental analysis of many samples was the nature of the substrate on which the particulate material was collected. Samples deposited on carbonaceous substrates, for example, were obviously not suited for in situ carbon analysis. A solution to this problem was found by transferring sample material from the "as received" substrate to one more suited to the proposed method of analysis. Experiments with the indium foil technique presented in Section 1.2 have shown that in nearly every case investigated no measurable quantity (i.e. <0.1 μg) of substrate was carried over to the indium foil. The one exception to this observation was glass quartz fiber. For this reason samples submitted on this substrate were suspended in water passed through a 10 μm nylon sieve and redeposited on 0.1 μm Nuclepore filters prior to transfer to indium foil.

Carbon-14 containing particulate material deposited on indium foils was subjected to energy dispersive x-ray fluorescence analysis in an EDAX system and Auger electron analysis in a JEOL JAMP-10 Scanning Auger Microprobe. The former technique

provided quantitative data on elements with atomic number, Z>10; detection limits down to about 1 μg were achievable under ideal circumstances. Auger electron analysis in the JAMP-10 provided quantitative data for elements with Z>2 on individual particles down to 1 μm in diameter; this corresponds to a detection limit equal to or better than 1 pg for most elements.

A few samples submitted for analysis were found to contain particles which could be removed with fine tipped tweezers. In this case quantitative x-ray fluorescence analysis is subject to unknown self-absorption corrections and flame atomic absorption spectrophotometry was used to provide quantitative analytical data for selected elements.

2.0 RESULTS

The samples investigated in this study are listed in Table 2.1. Details of the sample collection procedures are given in the references listed in the column headed "Comments". Some of these references also contain analytical data on the carbon-14 and gamma activity of each sample/4,5/ and the results ot particle size measurements by microfiltration or using an Andersen cascade impactor/4,6/. The remainder of this section is devoted to the detailed presentation of previously unreported analytical data for each sample.

2.1 Sample #1: A Unit 1 End-Fitting Removal Trough Extension Swipe

Sample #1 contained a dark brown material consisting of some large particles, up to 2 mm in diameter (Figure 2.1), together with many finer particles, averaging about 10 μm in diameter (Figure 2.2). The mean size of the active particles in Sample #1 was previously determined to be 8.5 ± 0.5 μm/4/.

The present investigations have shown that the larger particles in Sample #1 may be easily crushed to yield the finer grained material which appears yellowish orange in colour under high magnification (Figure 2.3).

The carbon-14 specific activity of Sample #1 was reported in Reference 4 to be 0.5 ± 0.3 Ci/g. This value was determined by an approximate autoradiographic procedure prior to the acquisition of a microbalance. New microbalance measurements have permitted the carbon-14 specific activity of Sample #1 to be re-determined by more reliable procedures. However, before reporting any specific activity data, attention should be drawn to the fact that all the samples investigated in this study were found to contain variable amounts of iron. Therefore, in order to compare the specific activities of different samples, it is necessary to correct sample weights for their iron content.

TABLE 2.1

CARBON-14 CONTAINING SAMPLES INVESTIGATED IN THIS STUDY

Sample #	Pickering Unit	Sample Description	Collection Date	Collection Substrate	Approx C-14 Content	Comments
1	1	An End-Fitting Removal Trough Extension Swipe	March/85	Cellulose Paper (subsequently suspended in L.S. Cocktail)	1 mCi	See /4/
2	2	Shock-Heating Airborne Particulate	April/85	Millipore Filter	2 μCi	See /9/
3	1	Shock-Heating Airborne Particulate	May/85	Millipore and Glass Fiber Filters	10 μCi	See /5/
4	1	Shock-Heating Airborne Particulate	May/85	Glass (Andersen Sampler Impactor Plates)	0.5 μCi	See /6/
5	2	End-Fitting Body (K11E) Swipes	Sept/85	Quartz Wool	1 mCi	Collected from End-Fittings Stored at CRNL
6	1	Channel P13 Annulus Bellows Debris	Oct/85	Silver Membrane	10 μCi	See /7/
7	1	Channel A13 Calandria Swipe	Jan/86	Foam Rubber Sponge	50 μCi	See /7/

Carbon-14 containing particles removed from Sample #1 were found by flame atomic absorption and x-ray fluorescence analysis to contain 50 ± 20% by weight of iron. It is probable that the iron is present mainly as ferric oxide, Fe_2O_3, or hydrated ferric oxide, FeOOH in view of the yellowish orange colour of the microparticles/10/.

In order to determine how much total carbon (carbon-12 + carbon-14) is associated with the iron-oxide particles, known weights of Sample #1 were heated to constant weight (~500° C) in a micro platinum boat. Based on duplicate measurements a weight loss of 15 ± 5% of the starting weight was recorded.

Auger electron analysis has shown particles from Sample #1 to contain iron, carbon, nitrogen and oxygen with carbon constituting 80 ± 10 atomic % of the ignitable material. When the above data are combined with the results of carbon-14 determinations by combustion and liquid scintillation counting the average carbon-14 specific activity of Sample #1 is found to be 0.15 ± 0.08 Ci/g of inactive carbon. This result indicates that only 3-4% of the carbon in Sample #1 is carbon-14.

The principal gamma activity associated with Sample #1 is Co-60 with a specific activity of 10 ± 5 μCi/g of iron oxide. (Note: The gamma activities previously reported for Sample #1 in Table 2.2 of Reference 4 should be in μCi and not in mCi.)

2.2 Sample #2: An Airborne Particulate Filter from a Unit 2 Shock-Heating

The operation of separating a pressure tube from the rolled joint connecting it to the end-fitting body is known as shock-heating and is a process which has resulted in the release of carbon-14 containing particulate to the reactor vault. Sample #2 was collected by J. Stephenson during shock-heating operations in the Unit 2 vault on April 27, 1985 /6/. Air was drawn through a 0.8 μm Millipore filter at a flow rate of two litres per minute for 6 hours. After this time the filter showed very little visible deposit but approximately 1.7 μCi of carbon-14 containing particulate was subsequently measured on the filter by gross β counting.

Optical microscopy of Sample #2 showed that the filter is covered with particles, mainly in the size range 2 μm to 20 μm, at a loading of about 8000/cm^2. Many of the particles exhibit an unusual branched structure ("Christmas trees"), (Figures 2.4 and 2.5). Low resolution autoradiography of the filter using Kodak NTB liquid emulsion (Figure 2.6) shows that the loading of active particles is about 5000/cm^2 or about 60% of the total

particle loading. That the sample activity is associated mainly with the branched particles is confirmed by inspection of autoradiographs at high magnification (Figure 2.7).

At very high resolution in a scanning electron microscope the branched particles exhibit two distinct morphologies: dendritic/11/ (Figure 2.8) and aciniform/12/ (Figure 2.9). However, both types of particle show essentially the same composition by Auger electron analysis, namely 75 ± 5 atomic % carbon, 20 ± 5 atomic % nitrogen and 5 ± 3 atomic % oxygen.

The procedure described in Reference 4 was used to estimate the specific activity of Sample #2 with the assumption that the particles consist of graphitic carbon of density 2.25 g/cm^3. On this basis the filter contains about 20 µg of active particulate and the carbon-14 specific activity is 0.08 ± 0.05 Ci/g of carbon.

Gamma spectrometry of Sample #2 showed traces of only two radionuclides, Co-60 and Sb-125, with time of count (Nov 19/85) activities of 0.68 ± 0.04 nCi and 0.15 ± 0.07 nCi per filter, respectively.

Energy dispersive x-ray analysis of Sample #2 detected 5 ± 2 µg of iron and traces (<0.5 µg) of copper, even though Auger analysis showed many iron-free particles in this sample.

2.3 Sample #3: Two Airborne Particulate Filters From a Unit 1 Shock-Heating

A series of airborne particulate filters was collected in the Unit 1 vault during shock-heating activities between May 25 and May 29, 1985. A summary of the gross γ/β and carbon-14 activities found on the filters and the associated airborne particulate activities has been reported by K. Curtis/5/.

For the present study two filters, a 0.45 µm Millipore and a GFA/E glass fiber, from high volume samplers were selected for more detailed investigations and are referred to jointly as Sample #3 in this report. The samplers were located directly in front of channel H8, where eleven shock heating cycles were carried out, and air was drawn through the samplers for 10 hours at a flow rate of 20 litres per minute for the Millipore filter and 100 litres per minute for the GFA/E glass fiber filter.

At the end of the sampling period the filters were covered with a light uniform greyish-black deposit. Optical microscopy revealed that both filters were heavily loaded with particles mainly in the size range 2 µm to 20 µm (Figures 2.10 and 2.11).

Several types of particles may be distinguished on the filters by their different colours or morphologies. The most abundant particles are black and generally amorphous or occasionally pyramidal in structure. Yellowish-orange or white, glassy particles are also quite common.

Analysis of material from the Millipore or GFA/E glass fiber filter in the Scanning Auger microprobe showed that the black pyramidal and the yellowish-orange particles are iron oxide contaminated with variable amounts of carbon. Their colour and morphology leave little doubt that the black pyramidal particles are magnetite (Fe_3O_4) and the yellowish-orange particles are ferric oxide (Fe_2O_3) or hydrated ferric oxide(FeOOH)/10/. Scanning electron micrographs of two large magnetite particles from Sample #3 are shown in Figures 2.12 and 2.13.

The average chemical composition of material from Sample #3 determined by Auger electron analysis of more than ten individual, randomly selected, particles is given in Table 2.2. (Auger electron concentration data are computer generated in atomic %, i.e. relative number of atoms, using pre-determined sensitivity factors. Weight % data, derived from atomic % values by a simple calculation, are also reported in Table 2.2 for convenience.)

TABLE 2.2

THE AVERAGE CHEMICAL COMPOSITION OF MATERIAL FROM SAMPLE #3 DETERMINED BY AUGER ELECTRON ANALYSIS

Element	Atomic %	Weight %
Carbon	36 ± 8	17 ± 4
Nitrogen	5 ± 3	3 ± 2
Oxygen	30 ± 5	19 ± 3
Silicon	2 ± 1	2 ± 1
Calcium	3 ± 2	5 ± 3
Iron	19 ± 4	42 ± 9
Nickel	1 ± 1	2 ± 2
Copper	3 ± 2	8 ± 5
Zinc	1 ± 1	2 ± 2

The results of the gamma spectrometric analysis of the two filters comprising Sample #3 are given in Table 2.3. The detection of 0.6 ± 0.2 nCi of the alpha-emitting radionuclide Am-241 in this sample indicates that approximately ten times the MPC_A of this species was present during sampling.

After gamma spectrometry approximately half of the Millipore filter was dissolved in a small volume (~10 mL) of acetone. By repetition of a centrifugation, decantation and resuspension procedure the cellulose from the Millipore filter was removed and the active material was left as a slurry in a few drops of acetone. The suspension was transferred by pipette to a tared micro weighing boat and heated to constant weight at 100°C. Gamma spectrometry showed that 60 ± 4% of the gamma active radionuclides on the original filter had been transferred to the weighing boat. The collected particulate, weighing approximately 230 µg, was ignited in air to bright red heat, cooled and reweighed; a loss of 52 ± 2 µg was measured corresponding to 23% of the unignited material.

TABLE 2.3

THE ACTIVITIES OF GAMMA ACTIVE RADIONUCLIDES IDENTIFIED IN SAMPLE #3 (TWO FILTERS)

Radionuclide	Time of Count (31 May/85) Activity (nCi)	
	Millipore Filter	GFA/E Glass Fiber Filter
Mn-54	0.99 ± 0.09	2.5 ± 0.2
Co-60	29.6 ± 0.3	71.0 ± 0.6
Zn-65	1.1 ± 0.2	2.2 ± 0.4
Zr-95	1.4 ± 0.1	3.3 ± 0.3
Nb-95	2.5 ± 0.1	5.4 ± 0.2
Ru-106	11.2 ± 0.7	19.5 ± 1.2
Sn-113	0.29 ± 0.07	0.67 ± 0.12
Sb-125	9.4 ± 0.2	20.9 ± 0.4
Cs-134	0.34 ± 0.08	1.1 ± 0.2
Cs-137	4.7 ± 0.1	10.8 ± 0.2
Ce-144	5.0 ± 0.2	13.2 ± 0.4
Eu-154	0.47 ± 0.09	1.5 ± 0.3
Am-241	0.40 ± 0.10	0.81 ± 0.12

Two subsamples, approximately 5 µg each, one from the Millipore filter and the other from the GFA/E glass fiber filter, were prepared on indium foils. The sub-samples were subjected to gamma spectrometric and energy dispersive x-ray fluorescence analysis and confirmed to be representative of the bulk material (i.e. ~50% (w/w) Fe; ~0.25 nCi Co-60). Combustion of the sub-samples in the Tri-Carb Oxidizer gave 0.24 ± 0.02 µCi of carbon-14. If the active material is assumed to contain 20 ± 5% inactive carbon the average carbon-14 specific activity of Sample #3 is 0.24 ± 0.09 Ci/g of carbon.

2.4 Sample #4: Andersen Sampler Plates from a Unit 1 Shock-Heating

The Andersen sampler is a cascade impactor for collecting size fractionated airborne particulate material/13/. The sampler consists of a stack of plates mounted in pairs through which air is drawn at a constant flow rate. The upstream plate, called a jet plate, has concentric circles of precision drilled orifices while a glass plate is mounted a few millimetres downstream to collect particles with effective aerodynamic diameters in a specified range. Seven collection stages are usually used covering the particle size range from 10 μm to 0.4 μm.

An Andersen sampler was positioned on the rolling shield during shock-heating activities in the Unit 1 vault between May 25 and May 29, 1985. J. Stephenson and M. Eisner have prepared an interim report on the data obtained by the Andersen sampler at this time/6/. For the present study some of the collector plates from the shock-heating of channel H17 carried out on May 26, 1985 were selected for further investigations and are referred to collectively as Sample #4 in this report.

Figures 2.14 and 2.15 are optical micrographs of material collected on Stage 4 of the Andersen sampler; the micrographs were taken with reflected and transmitted light, respectively. If clusters of particles are ignored the measured average particle size of 3 ± 1 μm is in reasonable agreement with the theoretical range of aerodynamic diameters, 3.3 μm - 2.2 μm, for Stage 4 of the sampler.

To clearly resolve individual particles on sampler Stages 6 and 7 magnifications in excess of 1000X are required. Figure 2.16 is a scanning electron micrograph of particles on Stage 6 of Sample #4. The measured average particle size of 1.0 ± 0.3 μm is again close to the theoretical range of aerodynamic diameters, 1.1 μm - 0.6 μm, for Stage 6 of the sampler.

The yellowish colour of some of the particles on the Andersen plates (see Figure 2.14) suggests the presence of ferric oxide in Sample #4. This was supported by the results of Auger electron analysis of material removed from Stages 6 and 7 as shown in Table 2.4. An average of 22 ± 4% (w/w) iron was detected in material from the two stages.

The results of the gamma spectrometric analysis of a complete Andersen plate (Stage 5) from Sample #4 are given in Table 2.5. Gross γ/β measurements indicated the presence of approximately 4.5 μCi of carbon-14 on the same Andersen plate (Stage 5); this is more than 1000 times the gross γ activity determined by summing the activities in Table 2.5.

TABLE 2.4

THE AVERAGE CHEMICAL COMPOSITION OF MATERIAL FROM SAMPLE #4 DETERMINED BY AUGER ELECTRON ANALYSIS

Element	Weight %	
	Stage 6	Stage 7
Carbon	53 ± 5	65 ± 6
Nitrogen	3 ± 2	3 ± 2
Oxygen	9 ± 3	6 ± 3
Iron	26 ± 4	18 ± 3
Copper	9 ± 3	8 ± 2

TABLE 2.5

THE ACTIVITIES OF GAMMA-ACTIVE RADIONUCLIDES IDENTIFIED ON STAGE 5 OF SAMPLE #4

Radionuclide	Time of Count (7 Aug/85) Activity (nCi)
Mn-54	0.07 ± 0.01
Co-60	1.44 ± 0.03
Zn-65	0.06 ± 0.02
Zr-95	0.02 ± 0.01
Nb-95	0.04 ± 0.01
Ru-106	0.65 ± 0.09

The combustion of 0.75 ± 0.05 µg of material transferred to indium foils from Stage 7 (duplicate measurements), yielded 40.0 ± 1.3 nCi of carbon-14; this corresponds to a carbon-14 specific activity of 0.05 ± 0.02 Ci/g of sample or 0.08 ± 0.02 Ci/g of carbon for material on Stage 7 of the Andersen sampler.

2.5 Sample #5: Swipes from a Unit 2 End-Fitting Body (K11E)

After the August 1, 1983, failure of a pressure tube in the Unit 2 reactor at Pickering NGS a number of pressure tubes and associated end-fittings were removed and sent to Chalk River Nuclear Laboratories for examination and long term storage in swimming-pool type storage bays.

In September 1985, at the request of Ontario Hydro Chemical Research, swipes were taken from the outer surface of the K11E pressure tube and end-fitting body and are referred to collectively in this report as Sample #5. The swipes were obtained with quartz wool swabs from:

(i) The carbon steel radiation sleeve.

(ii) The 403 stainless steel end-fitting body close to the radiation sleeve.

(iii) The 403 stainless steel end-fitting body close to the bearing sleeve journal ring.

(iv) The Zircaloy-2 pressure tube.

The swipes were taken from visible deposits which were black or silvery-grey in the case of the radiation sleeve and pressure tube and rusty orange or brown in the case of the end-fitting body.

The swipe from the end-fitting bearing sleeve journal ring registered in excess of 70 000 cpm of low energy β-radiation approximately 7 cm from an Eberline E-140 Geiger counter; this was at least three times higher than the activity found on any of the other swipes. Subsequent investigations of Sample #5 have therefore been restricted to the bearing sleeve journal ring swipe.

The swipe was suspended in a small volume of water (10 mL), ultrasonically shaken for two minutes, and passed through a 20 µm nylon sieve to separate the active material from its quartz wool substrate. Liquid scintillation counting of a 0.1 mL aliquot of the resulting suspension indicated that about 20 µCi of carbon-14 had been obtained from the swipe.

To collect the carbon-14, the suspension was passed through a 0.1 μm Nuclepore filter. The fact that only 0.2% of the β activity was found in the filtrate by liquid scintillation counting confirmed that the carbon-14 was present in an insoluble particulate form. Gamma spectrometric analysis of the Nuclepore filter also showed that only nCi quantities of gamma active radionuclides were associated with the carbon-14 as listed in Table 2.6.

TABLE 2.6

THE ACTIVITIES OF GAMMA-ACTIVE RADIONUCLIDES COLLECTED FROM SAMPLE #5 ON A 0.1 μm NUCLEPORE FILTER

Radionuclide	Time of Count (27 Jan/86) Activity (nCi)
Mn-54	1.32 ± 0.02
Co-60	26.18 ± 0.05
Zn-65	0.11 ± 0.03
Zr-95	0.02 ± 0.01
Nb-95	0.04 ± 0.01
Sb-125	0.13 ± 0.03

Figures 2.17 and 2.18 are optical micrographs of the material deposited on the Nuclepore filter. It consists of a mixture of black and yellow particles with the former always being found in association with the latter. Smaller amounts of white, orange or red coloured particles are also discernable in Sample #5 but these generally occur without accompanying black particles. The black particles are mainly in the size range 1 μm - 5 μm.

X-ray fluorescence analysis of the material from Sample #5 detected only iron with traces of silicon (possibly from residual quartz wool fibers), copper and chromium. Examination of material from this sample in the Scanning Auger Microprobe confirmed the presence of iron and showed also the presence of oxygen, carbon and nitrogen. The results of quantitative Auger electron analysis of Sample #5 are given in Table 2.7. An electron micrograph of material from the Nuclepore filter (Figure 2.19) shows its highly amorphous or microcrystalline nature.

A comparison of material from Sample #5 with corrosion deposits formed on steel coupons shows that the yellow particles are almost certainly hydrated iron oxide/14/. In order to separate a carbon-14 containing component from the hydrated iron oxide associated with it, material from Sample #5 was suspended in a small volume (~25 mL) of 4 N HCl for 30 minutes and then passed through a 0.1 μm Nuclepore filter. Only 0.5% of the initial carbon-14 activity passed into solution while 90% of the iron, as indicated by Co-60, dissolved. An optical micrograph of the material retained by the Nuclepore filter after the HCl treatment, Figure 2.20, showed mainly small (1 μm - 5 μm) black particles.

TABLE 2.7

THE AVERAGE CHEMICAL COMPOSITION OF MATERIAL FROM SAMPLE #5 DETERMINED BY AUGER ELECTRON ANALYSIS

Element	Weight %
Carbon	30 ± 3
Nitrogen	2 ± 2
Oxygen	15 ± 3
Iron	53 ± 6

Carbon-14 specific activity measurements were carried out on Sample #5 by the combustion of sub-samples as discussed in Section 1.2. A value of 0.06 ± 0.01 Ci/g of material was determined for the untreated sample, i.e. carbon plus hydrated iron oxide. Because the sample contains 30 ± 3% (w/w) of carbon (see Table 2.7) the carbon-14 specific activity is 0.20 ± 0.05 Ci/g of carbon. Measurements on Sample #5 after the removal of iron oxide by HCl yielded a carbon-14 specific activity of 0.24 ± 0.06 Ci/g of material, estimated to be at least 90% carbon, in good agreement with the above result.

2.6 Sample #6: Filters from the Vacuuming of Unit 1 Channel P13 Annulus Bellows

The end-fitting body is connected to the end-shield lattice tube by an inconel 600 metal bellows. The annulus bellows, by virtue of their convoluted structure, are favourable areas for the accumulation of debris resulting from retubing operations. For this reason attempts were made to collect samples of material from the annulus bellows at Pickering after the completion of shock-heating operations in mid 1985. The samples investigated

in the present study were obtained by E. Koehl in October 1985 by vacuuming in several bellows and their adjacent lattice tubes on the west reactor face of Unit 1 and collecting the dislodged particulate material on cellulose or silver membrane filters. The material deposited on the silver membrane filter was taken exclusively from channel P13 and is referred to in this report as Sample #6.

Sample #6 consisted of a moderately heavy blackish deposit which registered in excess of 70 000 cpm of low energy β-radiation a few centimetres from a Geiger counter. Gamma spectrometric analysis of Sample #6 showed very little gamma activity as indicated by Table 2.8. Close inspection of the blackish deposit revealed specks of a white material mixed with a brownish-black powder; some metallic particles, up to 2 mm in diameter were also visible.

TABLE 2.8

THE ACTIVITIES OF GAMMA-ACTIVE RADIONUCLIDES IDENTIFIED IN SAMPLE #6

Radionuclide	Time of Count (31 Oct/85) Activity (nCi)
Mn-54	0.1 ± 0.1
Co-60	2.1 ± 0.1
Sb-125	1.5 ± 0.1

It proved useful for identification purposes to view the same groups of particles from Sample #6 by both optical and electron microscopy; such micrograph pairs are shown in Figures 2.21 to 2.26. (It should be noted that the magnifications of the optical and electron micrographs are slightly different and the orientations do not always exactly correspond. In addition, the superior depth of field of the electron micrographs is immediately apparent.)

The filamentous particles illustrated in Figures 2.23 and 2.24 are undoubtedly the most striking feature of Sample #6. Auger electron analysis has shown that these unusual particles are essentially pure cadmium oxide, CdO, or occasionally cadmium oxide covered with a thin layer of carbon. When carbon is

detected on these particles it is always readily removed by less than 1 minute of argon-ion sputtering, showing that the carbon is present as a surface layer less than 0.1 μm thick. Additional confirmation of the identity of these particles is provided by literature reports of the unusual whisker or needle-like morphologies exhibited by vapour deposited cadmium oxide/15/.

A search for the probable origin of cadmium oxide in the Pickering Unit 1 annulus gas system has led to the conclusion that it is produced by the oxidation of a brazing alloy, known to contain over 20% (w/w) of cadmium, used in the fabrication of the shock-heating probe. The absence of cadmium oxide in the other samples investigated in this report suggests that cadmium is not a major constituent of typical gas annulus particulate material but may occur at significant levels in localized deposits as a result of shock-heating.

X-ray fluorescence analysis of small portions (10 - 100 μg) of Sample #6 failed to detect more than traces of cadmium confirming its low average abundance; the other elements detected by this technique, and their concentrations, are reported in Table 2.9.

TABLE 2.9

THE AVERAGE CHEMICAL COMPOSITION OF MATERIAL FROM SAMPLE #6 DETERMINED BY ENERGY DISPERSIVE X-RAY ANALYSIS

Element	Weight %
Chromium	8 ± 5
Iron	84 ± 4
Nickel	2 ± 2
Copper	6 ± 2

Auger electron analysis of amorphous deposits from Sample #6, such as those shown in Figures 2.21 and 2.22, detected only carbon, nitrogen, oxygen and iron in the proportions reported in Table 2.10.

TABLE 2.10

THE AVERAGE CHEMICAL COMPOSITION OF AMORPHOUS DEPOSITS FROM SAMPLE #6 DETERMINED BY AUGER ELECTRON ANALYSIS

Element	Weight %
Carbon	20 ± 6
Nitrogen	2 ± 2
Oxygen	22 ± 4
Iron	56 ± 10

The combustion of known weights of material from Sample #6 gave an average carbon-14 concentration of 0.039 ± 0.004 Ci/g of sample; if the average carbon content of Sample #6 is assumed to be 20 ± 6% (w/w), the carbon-14 specific activity is 0.20 ± 0.08 Ci/g of carbon.

2.7 Sample #7: A Unit 1 Calandria Swipe (A13)

After the removal of a pressure tube the empty channel is cleaned by pushing wetted foam rubber sponges through the calandria tube. In order to also clean the inside of the end-fitting body two different size sponges are used, one approximately 14 cm in diameter and the other 18 cm in diameter.

A pair of sponges from the cleaning of channel A13 of the Pickering Unit 1 reactor was sent to Chemical Research in January 1986 and is referred to in this report as Sample #7 . Calandria swipes from Pickering Unit 1 and Bruce Unit 2 have been investigated previously by Chemical Research and the results reported in References 16 and 17.

The "as-received" sponges were subjected to gamma spectrometric analysis and the radionuclides listed in Table 2.11 were quantitatively determined. It is evident from the data in Table 2.11 that Sample #7 contains considerably more gamma activity than the other samples investigated in this report. For this reason it was considered worthwhile to make a determination of alpha-active radionuclides in Sample #7 the results of which are given in Table 2.12.

The leading edge of both sponges showed a blackish discolouration where most of the activity was concentrated. A strip of sponge, 4 cm long and 1 cm wide, was cut from the blackened area

of the 14 cm diameter sponge and placed in a small volume (~25 mL) of water. Particulate material was shaken loose from the strip by ultrasonic agitation and subsequently redeposited onto a 0.1 μm Nuclepore filter. Small sub-samples of particulate material (10 - 100 μg) were taken from the Nuclepore filter using tared indium foils. These were subjected to gamma spectrometric and energy dispersive x-ray analysis.

It was found that, judging by activity ratios, far more Zircaloy-2 derived activated corrosion products (Zr-95, Nb-95, Sn-113, Sb-125) than steel derived activated corrosion products (Mn-54, Co-60), were collected on the Nuclepore filter or picked up by the indium foils. For example, a foil with 129 μg of material ultrasonically removed from the 14 cm sponge was found to have 3% of the initial Zr-95 and Nb-95 activities but only 0.1% of the Co-60 and Mn-54 activities.

Microscopic examination of the indium foils showed essentially three types of deposited material:

(i) Yellow or orange amorphous particles up to 10 μm in diameter.

(ii) Black amorphous or regular triangular particles up to 50 μm in diameter (See Figure 2.27).

(iii) White platelet-like particles up to 300 μm in diameter (see Figure 2.28).

Subsequent investigations using the scanning Auger Microprobe have shown these particles to be hydrated ferric oxide (FeOOH), magnetite (Fe_3O_4) and zirconium oxide (ZrO_2), respectively. It appears that the large zirconium oxide platelets are readily removed from the sponge resulting in an enrichment of zirconium on the indium foil sub-samples.

In order to obtain a truly representative sub-sample of particulate material from the calandria swipe a 1 cm x 1 cm x 0.5 cm piece was cut from the "as-received" 14 cm sponge and burnt in air (with CO_2 trapping). The residue was subjected to energy dispersive X-ray analysis, the results of which are reported in Table 2.13. By comparison sub-samples of the calandria swipe, prepared as previously described on indium foils, contained up to five times the concentration of zirconium reported in Table 2.13.

TABLE 2.11

THE ACTIVITIES OF GAMMA-ACTIVE RADIONUCLIDES IDENTIFIED IN SAMPLE #7

Radionuclide	Time of Count (Jan 8/86) Activity (nCi)	
	14 cm Sponge	18 cm Sponge
Mn-54	86 ± 5	34 ± 4
Co-60	5450 ± 20	2196 ± 9
Zn-65	580 ± 10	940 ± 10
Zr-95	87 ± 9	24 ± 6
Nb-94	16 ± 4	4 ± 2
Nb-95	157 ± 5	44 ± 3
Ru-106	590 ± 40	260 ± 20
Sn-113	47 ± 5	12 ± 3
Sb-125	4290 ± 30	1300 ± 10
Cs-134	45 ± 5	23 ± 4
Cs-137	249 ± 5	130 ± 4
Ce-144	420 ± 20	200 ± 20
Eu-154	35 ± 6	17 ± 3
Am-241	31 ± 7	13 ± 3

TABLE 2.12

THE ACTIVITIES OF ALPHA-ACTIVE RADIONUCLIDES IDENTIFIED IN SAMPLE #7 (14 cm SPONGE)

Radionuclide	Time of Count (Mar 28/86) Activity (nCi)
Pu-238	14 ± 3
Pu-239 + Pu-240	60 ± 9
Am-241	31 ± 7
Cm-242	1.5 ± 0.3
Cm-244	13 ± 2

TABLE 2.13

THE AVERAGE CHEMICAL COMPOSITION OF MATERIAL FROM SAMPLE #7 DETERMINED BY ENERGY DISPERSIVE X-RAY ANALYSIS

Element	Weight %
Aluminum	1 ± 1
Silicon	1 ± 1
Calcium	3 ± 2
Iron	60 ± 14
Copper	18 ± 6
Zinc	13 ± 5
Zirconium	4 ± 4

The distribution of carbon in Sample #7 was investigated by Auger electron analysis with argon-ion sputtering. Both the iron oxide and zirconium oxide particles in their "as-received" condition showed the presence of carbon. However, carbon could be completely sputtered off the surface of the zirconium oxide particles in about 10 minutes while the iron oxide particles showed only a 25% reduction in carbon for the same sputtering interval. From the known sputtering rate of about 20 nm/min the carbon layer on the zirconium oxide is estimated to be only about 0.2 μm thick.

It proved possible to remove individual particles of zirconium oxide, weighing as little as 15 μg, from the 14 cm diameter sponge; these particles showed weight losses of no more than 1% of their initial weight on ignition in air, confirming the low abundance of carbon on the zirconium oxide particle surfaces. As expected, there are correspondingly low levels of carbon-14 associated with the zirconium oxide particles; typically only 0.15 ± 0.05 mCi/g of ZrO_2.

The material ultrasonically shaken from the 14 cm diameter calandria swipe and therefore enriched in zirconium oxide (estimated to contain 20 ± 5% Zr (w/w) and 40 ± 10% Fe (w/w) by x-ray analysis), gave 0.5 ± 0.1 mCi of carbon-14/g of sample. By comparison the combustion of a piece of calandria swipe sponge yielded 1.0 ± 0.2 mCi of carbon-14/g of combustion residue. These results suggest that the carbon-14 present in Sample #7 is preferentially associated with iron oxide particles.

3.0 SUMMARY AND DISCUSSION

Table 3.1 summarizes the salient features of the chemical and radiochemical data obtained for the samples investigated in this study. Data for Sample #7 are not included in Table 3.1 because of the analytical problems associated with carbon determinations for this sample as discussed in Section 2.7. If all the chemical and physical characteristics that are common to the samples investigated to date are considered, a reasonably consistent picture emerges of the carbon-14 containing particulate material in the Pickering Unit 1 and 2 gas annulus systems and is discussed below.

3.1 Physical, Chemical and Radiochemical Properties

The material consists of a fine black powder which is readily dispersed due to its small particle size and tendency to become electrostatically charged. Carbon, nitrogen, oxygen and iron account for at least 90% of its mass. The remaining 5 - 10% of the material is made up of elements such as copper, zinc, calcium and silicon believed to stem from extraneous sources such as vault dust, shock-heating probe debris, etc. No information is currently available on the hydrogen (or deuterium) content of the material.

The iron occurs in the material in combination with oxygen mostly as ferric oxide, Fe_2O_3 or hydrated ferric oxide, FeOOH, but occasionally as magnetite, Fe_3O_4. These oxides of iron are essentially contaminants stemming from steel corrosion products in the gas annulus system. The ferric oxide imparts an orange or yellowish colour to many of the particles when viewed under a microscope. It is, of course, quite possible that some of the observed iron oxide was formed in the gas annulus system after reactor shutdown.

The carbon, of which only about 4% is carbon-14 and the remainder inactive carbon-12, is mixed with the iron oxides in the form of discrete carbonaceous particles in the size range 1 - 10 μm. The precise chemical speciation of these carbon rich particles remains uncertain. However, the chemical properties of the particles such as their insolubility in water, organic solvents, mineral acids or ammonia, and their thermal stability (to at least 350°C) suggest that they are akin to the polymeric carbon particles found in soots or carbon black. Certain other properties of the particles, such as their propensity to adhere to metal or glass surfaces, suggest that the polymeric carbon may have active sites probably due to nitrogen, oxygen or hydrogen containing functional groups.

TABLE 3.1

SUMMARY OF ANALYTICAL DATA OBTAINED FOR SIX SAMPLES OF CARBON-14 CONTAINING PARTICULATE MATERIAL FROM PICKERING GAS ANNULUS SYSTEMS

Sample #	Pickering Unit	Chemical Composition (Weight %)				Radiochemical Composition		Carbon Isotope Ratio
		Carbon	Nitrogen	Oxygen	Iron	Carbon-14 Ci/g of Sample	Carbon-14 Ci/g of Carbon	$\left(\frac{C\text{-}14}{C\text{-}12} \times 100\right)$
1	1	15	2	25	50	0.023	0.15	3.4
2	2	45	9	15	25	0.036	0.08	1.8
3	1	17	3	19	42	0.041	0.24	5.4
4	1	59	3	8	22	0.047	0.08	1.8
5	2	30	2	15	53	0.072	0.24	5.4
6	1	20	2	22	56	0.040	0.20	4.5
Average	-	31 ± 14	4 ± 2	17 ± 5	41 ± 12	0.043 ± 0.011	0.17 ± 0.06	3.7 ± 1.4

The average carbon -14 activity in the particulate material is estimated to be 0.04 ± 0.01 Ci/g of sample or 0.17 ± 0.06 Ci/g of carbon. The latter figure indicates that only about 4% of the carbon in the material is carbon-14, the majority being inactive carbon-12. The origin of carbon-12 in the samples remains uncertain although there are potentially many sources of inactive carbon in a gas annulus system, e.g. impurities in the nitrogen make-up gas, metal surface contaminants, etc. Nonethe-less the specific activity of the carbon-14 in the particulate material is very high and this contributes to the ease with which surfaces are contaminated by exposure to the material. For example, a simple calculation shows that, with the specific activities quoted above, only 5 μg of the material deposited on a 10 cm^2 surface is needed to register 50 000 cpm on contact with a 2.5% efficient Geiger counter; if this material is distributed uniformly on the surface it constitutes a layer only about 15 atoms thick. At the same time the decontamination of such a surface deposit would be difficult given the observed insolubility of carbon-14. A report is in preparation discussing the results of long term carbon-14 leaching experiments carried out at Chemical Research/18/.

The slight gamma activity associated with the particulate material is principally due to Co-60 with smaller amounts of Sb-125, Mn-54, Zn-65, etc. The Co-60 is generally present at a concentration of about 0.05 mCi/g of sample or 0.1 mCi/g of iron oxide. The latter value is comparable to the Co-60 specific activity in primary heat transport (PHT) corrosion particulate (crud). It is probable that PHT system crud is not normally present in the gas annulus system but enters in small amounts during retubing operations. The very low levels of alpha activity found in some samples are also probably introduced in the same way.

In conclusion, it should be noted that if any other radionuclides, e.g. Ni-63, Zr-93, Sn-121m, are present in the Pickering Unit 1 and 2 gas annulus system samples besides those already mentioned, their present specific activities are less than 50 μCi/g. This result is based on gross γ/β measurements of the residues remaining after the combustion of particulate material submitted to Chemical Research.

3.2 The Distribution of Carbon-14 Containing Particulate Material in the Pickering Gas Annulus Systems and the Mechanism of its Deposition

Although sufficient data are not available to give a complete account of the distribution of the carbon-14 containing particulate material in a Pickering gas annulus system, some useful conclusions may be drawn from the samples investigated so far. One such conclusion, for example, is that a significant quantity

of the carbon-14 is deposited out of core even though it is all produced in core. As discussed in Section 2 of this report, the calandria tube and pressure tube swipe samples failed to yield large quantities of carbon-14 compared with similar swipes of the end-fitting bodies. The sampling procedures may be partly responsible for this difference, especially if the carbon-14 adheres to a Zircaloy surface more readily than a steel surface, but there is no reason to expect such behaviour. It therefore appears that carbon-14, produced in core by the $^{14}N(n,p)^{14}C$ reaction, is deposited primarily on the surface of the end-fitting bodies or possibly on the adjacent lattice tubes, a region inaccessible to sampling.

Especially heavy carbon-14 containing deposits have been found in the vicinity of the end-fitting bearing sleeve, an area on the periphery of the reactor core, suggesting that the hot carbon-14 atoms are not significantly adsorbed by metal surfaces until they have diffused out of the high neutron and gamma flux occurring in the reactor core. A detailed examination of a pressure tube surface would be needed to determine the distribution of carbon-14 in core.

The association of carbon-14 with ferric oxide particles is also a significant feature of the Pickering gas annulus samples. It implies that a connection may exist between carbon-14 deposition and the formation of ferric oxide on steel surfaces. The inter-dependence of steel corrosion and carbon deposition has, in fact, been observed in gas cooled reactors and results in a phenomenon known as "breakaway" oxidation/19/. A literature survey shows that there is an abundance of data on the deposition of carbon from CO_2 in advanced gas reactors/20/, while several reports have considered the effects of contaminants such as H_2, H_2O, CO, CO_2, CH_4, etc. in helium cooled reactors/21,22/. Unfortunately nitrogen is not widely used in nuclear systems and has therefore not been fully investigated with respect to carbon deposition/23/. None-the-less, if nitrogen is considered to be chemically similar to an inert gas, an extrapolation of the experimental results for helium to a nitrogen system should have some validity.

The results reported by Everett et al in Reference 21 are particularly interesting in this context since these workers observed that deposits formed in helium cooled reactors always consist of a carbonaceous material mixed with a magnetic form of iron. (A recent re-investigation of the samples from Pickering has shown that, in the few cases where sufficient material is available to make measurements, at least some of the Unit 1 samples are also magnetic.) No definitive conclusions were made in Reference 21 as to the nature of the carbonaceous deposits

found in helium cooled reactors, it was however speculated that carbon deposition occurs primarily through the catalytic action of iron carbide intermediates. (More recent investigations suggest that γ-Fe_2O_3 may be the active catalyst/24/.)

While the comparison of carbon deposition in nitrogen, where very little experimental data exist, with a relatively well studied system such as helium is very useful, it should be remembered that nitrogen is potentially far more reactive than helium. Indeed, an average of 4% (w/w) nitrogen has been found in the Pickering gas annulus samples confirming that nitrogen is not entirely an inert gas with regard to carbon deposition reactions. Certainly the reaction between molecular nitrogen and solid carbon is thermodynamically not feasible in the temperature range from 25°C to 300°C, but solid carbon does react rapidly with active nitrogen, due to the presence of metastable nitrogen atoms, forming cyanogen gas C_2N_2 or solid paracyanogen $(CN)_n$.

Because active nitrogen and carbon-14, are produced by the radiolysis of molecular nitrogen/25/, it appears probable that some ^{14}CN containing species are formed in the nitrogen gas annulus system during reactor operation/26/. B.A. Ryan at Hanford Research Laboratories investigated the radiation-induced reaction of graphite with nitrogen and reported finding traces of cyanogen in the gas phase as well as a yellow-brownish deposit, believed to be paracyanogen, on the walls of the reaction vessel/27/. Similarly, S. Veprek observed the deposition of mixtures of carbon and paracyanogen in a high frequency discharge between graphite electrodes in a nitrogen atmosphere/28/, while D.R. Safrany et al reported the formation of a brown-black polymer, presumably also paracyanogen, in the reaction of active nitrogen with hydrocarbons/29/.

The chemical and physical properties of paracyanogen have been described by L.L. Bircumshaw et al/30/. It is a brownish-black polymeric material which is essentially unaffected by mineral acids and most organic solvents. It is thermally stable to at least 450° C.

It is postulated that a carbon-14 containing polymer, similar to paracyanogen $(CN)_n$, has been formed in the Pickering 'A' gas annulus systems. It is further proposed that this species deposits on surfaces, especially at the periphery of the reactor core. This proposal is supported by the work of J.J. Cuomo et al who reported that paracyanogen films are formed on inert substrates placed outside of the reaction zone in the reactive rf sputtering of carbon in nitrogen/31/.

Some gas annulus steel surfaces may be subject to breakaway corrosion producing iron oxide particles which could be mobilized by shock-heating operations. These oxide corrosion products, and any other inert particles finding their way into the gas annulus system from sources such as carbon vane pumps or vault dust, could then act as carriers for the $(^{14}CN)_n$ polymer.

4.0 CONCLUSIONS AND RECOMMENDATIONS

The carbon-14 containing particulate material from the Pickering Unit 1 and 2 gas annulus systems is essentially a mixture of finely divided iron oxide corrosion products and a less well characterized species best described as a carbonaceous polymer. It appears that the carbon-14 containing polymer is not chemically combined with iron and that most, if not all, of the oxygen detected in the material is accounted for by the iron oxide which presumably acts as an inert substrate for the carbon containing species.

Measured carbon-14 specific activities (~0.2 Ci/g) are well below those expected for pure carbon-14 (~4 Ci/g) but are far in excess of any other activities associated with the material. Some of the particulate material's mass may be made up of unmeasured contributions from hydrogen or deuterium atoms while nitrogen generally contributes about 4% of the sample mass. It appears that the carbon-14 is chemically combined only to other carbon atoms or to nitrogen in a species resembling paracyanogen $(CN)_n$.

Preliminary investigations indicate that small fractions of the material are somewhat volatile or soluble in aqueous solvents but the majority of the active material is quite inert, stable in vacuo to at least 350°C and highly insoluble in common organic or aqueous inorganic solvents.

It is also quite possible that the carbon-14 containing species is in fact a complex mixture of carbon compounds formed at different locations in, or during different operational conditions of, the gas annulus system.

It is recommended that additional studies should be carried out to further elucidate the nature of the carbon-14 containing deposits in Hydro's nitrogen gas annulus systems. This work should include, but not be limited to:

(i) A confirmation of the C-14/C-12 ratios estimated in this report. A technique such as IR laser spectroscopy is ideal for precise and unambiguous measurements of the C-14/C-12 ratio of the material's combustion products.

(ii) A determination of the hydrogen (or deuterium) content of the active particulate material (e.g. by measurements of H_2O or D_2O in the material's combustion products).

(iii) A confirmation of the presence of ^{14}CN groupings in the active species by mass spectrometric or other investigations of pyrolysis products.

(iv) An investigation of the reasons for the observed association of the active material with iron oxide.

(v) An investigation of the chemistry of the carbon-14 containing material directed towards the development of decontamination processes for the removal of carbon-14 containing deposits.

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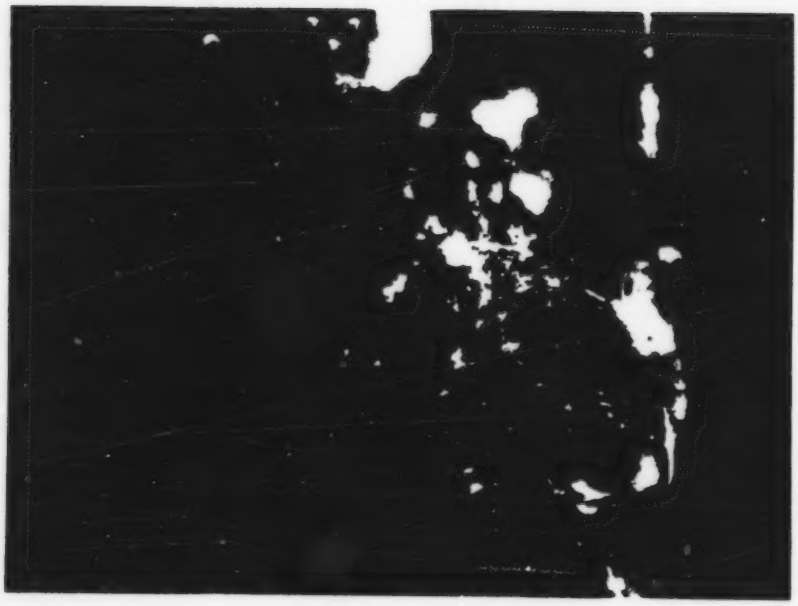

FIGURE 2.1 A LARGE PARTICLE FROM SAMPLE #1 (MAGNIFICATION 100X)

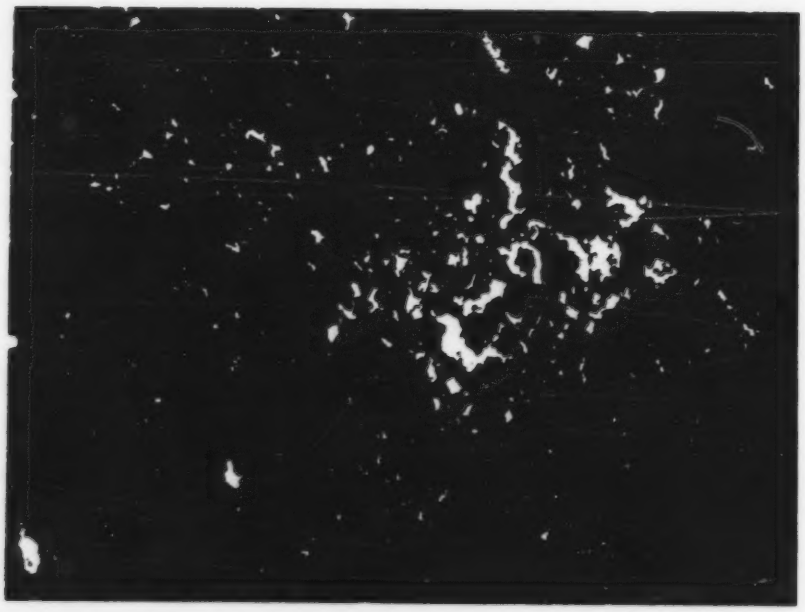

FIGURE 2.2 SMALL PARTICLES FROM SAMPLE #1 (MAGNIFICATION 200X)

FIGURE 2.3 SMALL PARTICLES FROM SAMPLE #1 (MAGNIFICATION 400X)

FIGURE 2.4 BRANCHED PARTICLES ("CHRISTMAS TREES") FROM SAMPLE #2 (MIGNIFICATION 600X)

FIGURE 2.5 BRANCHED PARTICLES (CHRISTMAS TREES") FROM SAMPLE #2 (MAGNIFICATION 600X)

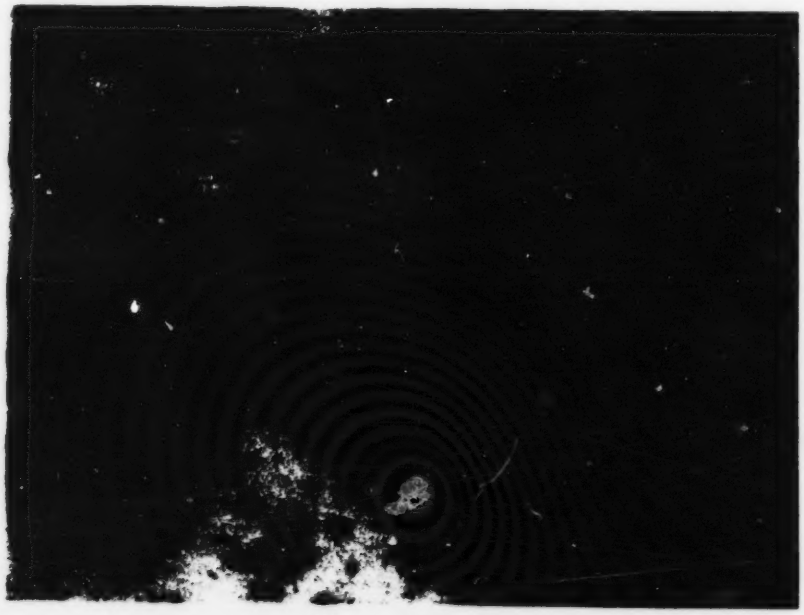

FIGURE 2.6 A LOW RESOLUTION AUTORADIOGRAPH OF SAMPLE #2 (MIGNIFICATION 50X)

FIGURE 2.7 A HIGH RESOLUTION AUTORADIOGRAPH OF SAMPLE #2 (MAGNIFICATION 600X)

FIGURE 2.8 AN ELECTRON MICROGRAPH OF A DENDRITIC PARTICLE FROM SAMPLE #2 (MAGNIFICATION 7000X)

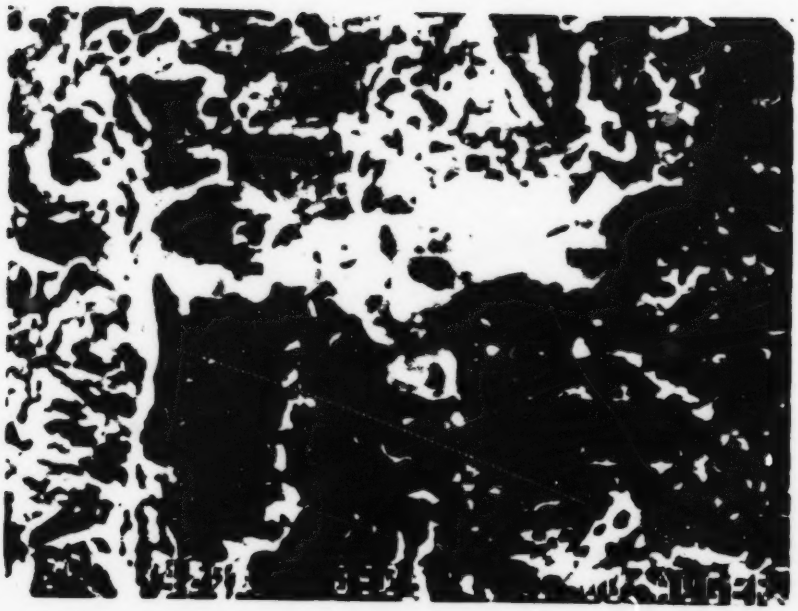

FIGURE 2.9 AN ELECTRON MICROGRAPH OF AN ACINIFORM PARTICLE FROM SAMPLE #2 (MAGNIFICATION 4500X)

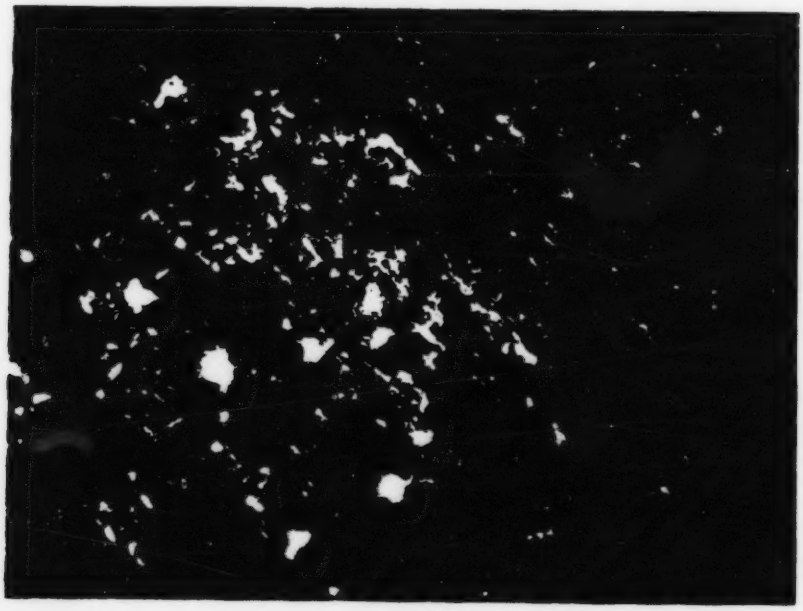

FIGURE 2.10 PARTICLES FROM SAMPLE #3 (MAGNIFICATION 400X)

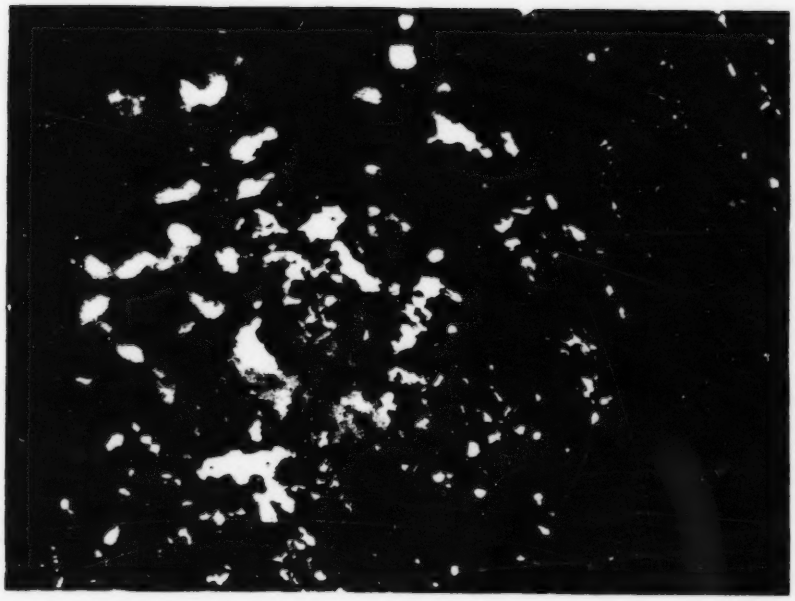

FIGURE 2.11 PARTICLES FROM SAMPLE #3 (MAGNIFICATION 400X)

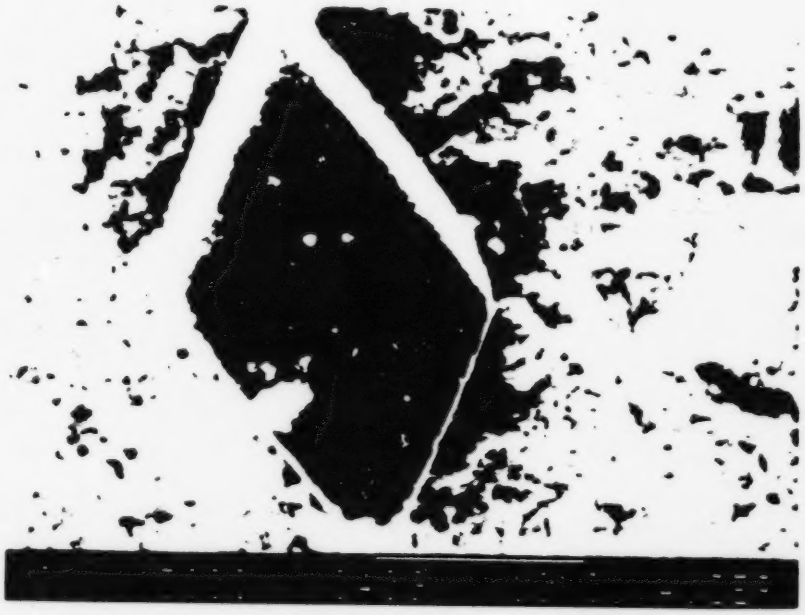

FIGURE 2.12 AN ELECTRON MEICROGRAPH OF A MAGNETITE PARTICLE FROM SAMPLE #3 (MAGNIFICATION 3000X)

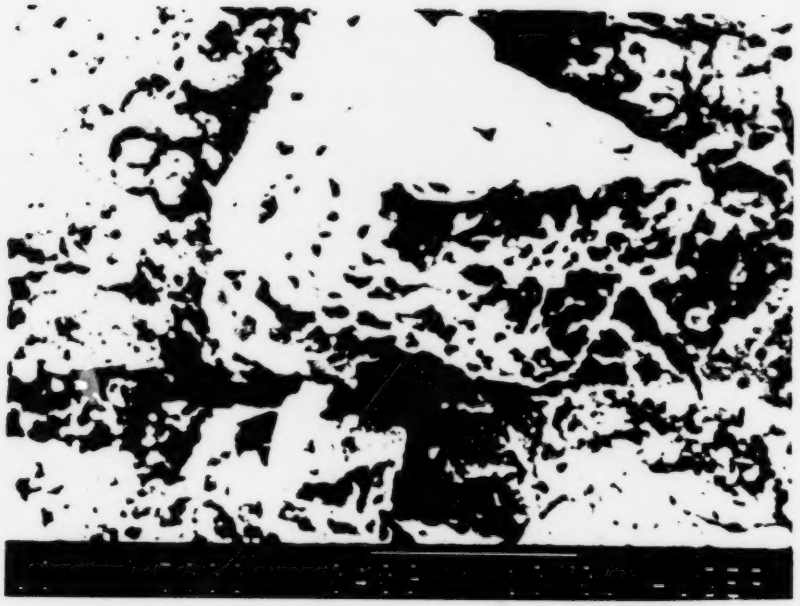

FIGURE 2.13 AN ELECTRON MICROGRAPH OF A MAGNETITE PARTICLE FROM SAMPLE #3 (MAGNIFICATION 3000X)

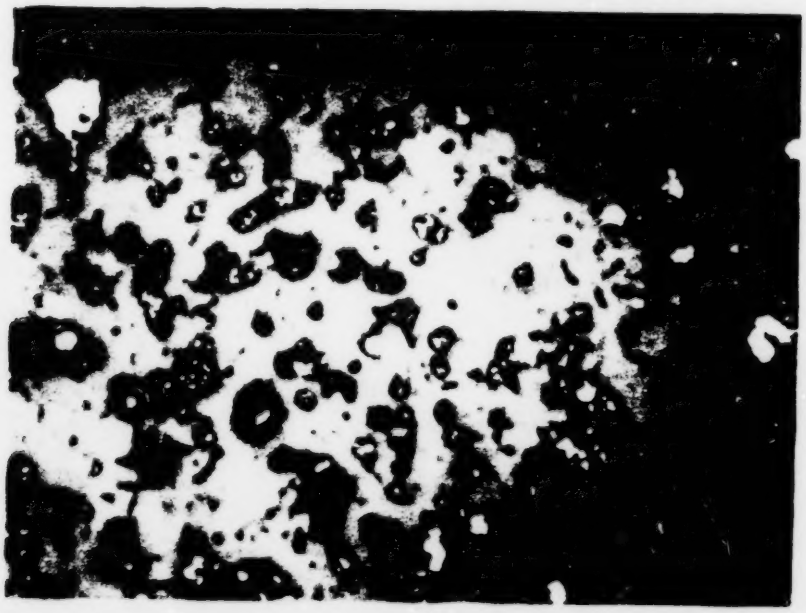

FIGURE 2.14 PARTICLES FROM SAMPLE #4 (MAGNIFICATION 1000X) (STAGE 4, REFLECTED LIGHT)

FIGURE 2.15 PARTICLES FROM SAMPLE #4 (MAGNIFICATION 1000X) (STAGE 4, TRANSMITTED LIGHT)

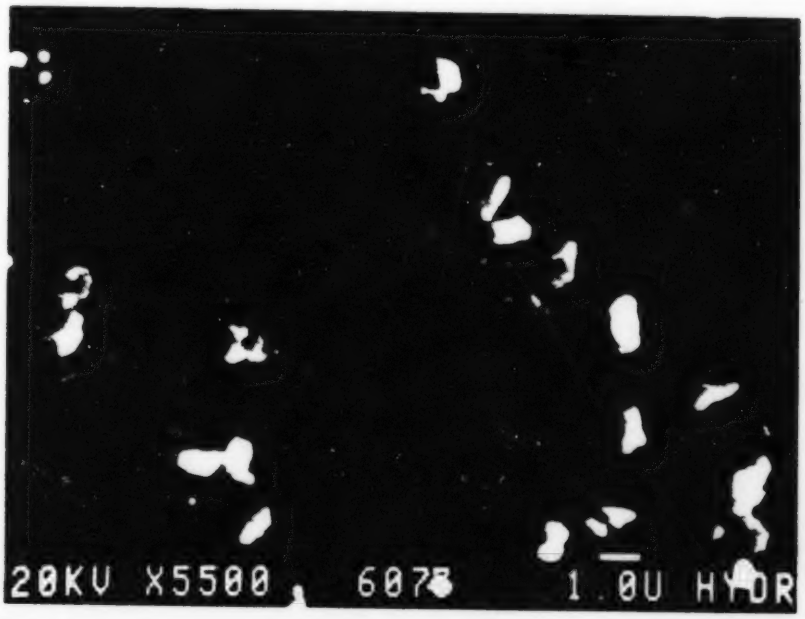

FIGURE 2.16 AN ELECTRON MICROGRAPH OF PARTICLES FROM SAMPLE #4 (MAGNIFICATION 5500X) (STAGE 6, 1.1 μm-0.6 μm AERODYNAMIC DIAMETER)

FIGURE 2.17 PARTICLES FROM SAMPLE #5 (MAGNIFICATION 1000X)

FIGURE 2.18 PARTICLES FROM SAMPLE #5 (MAGNIFICATION 1000X)

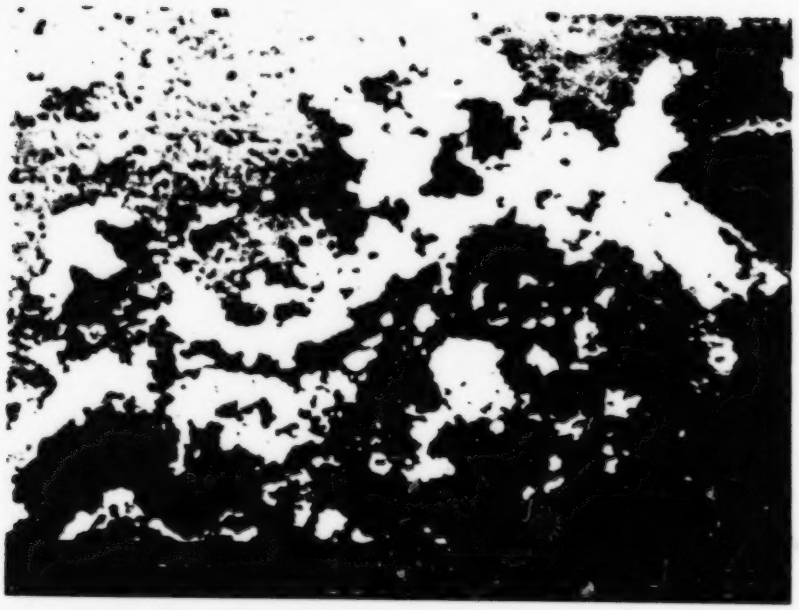

FIGURE 2.19 AN ELECTRON MICROGRAPH OF PARTICLES FROM SAMPLE #5 (MAGNIFICATION 3000X)

FIGURE 2.20 PARTICLES FROM SAMPLE #5 AFTER TREATMENT WITH HCL (MAGNIFICATION 600X)

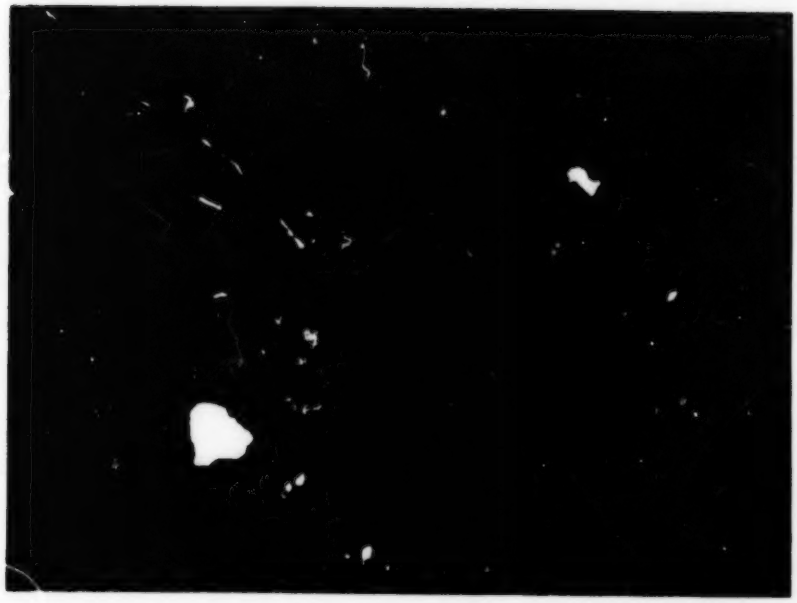

FIGURE 2.21 PARTICLES FROM SAMPLE #6 (MAGNIFICATION 400X)

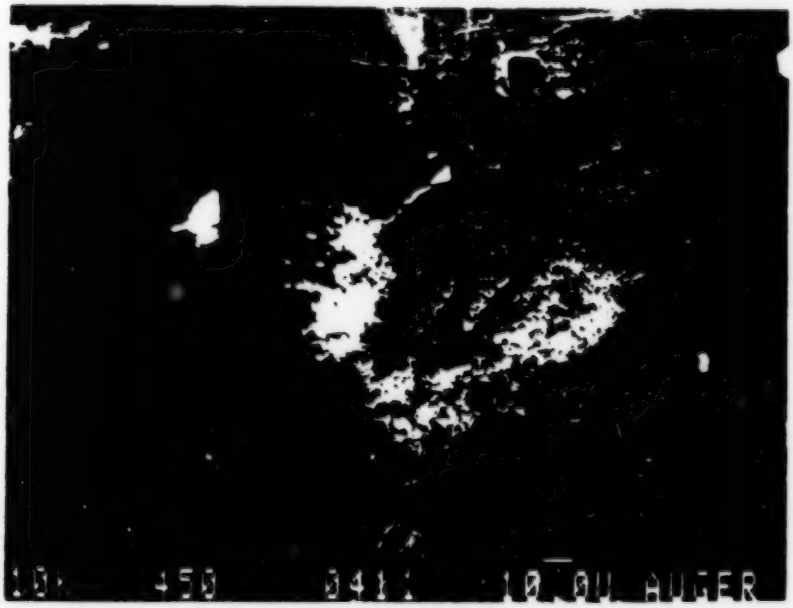

FIGURE 2.22 AN ELECTRON MICROGRAPH OF THE PARTICLES FROM SAMPLE #6 SHOWN IN FIGURE 2.21 (MAGNIFICATION 450X)

FIGURE 2.23 CADMIUM OXIDE PARTICLES FROM SAMPLE #6 (MAGNIFICATION 400X)

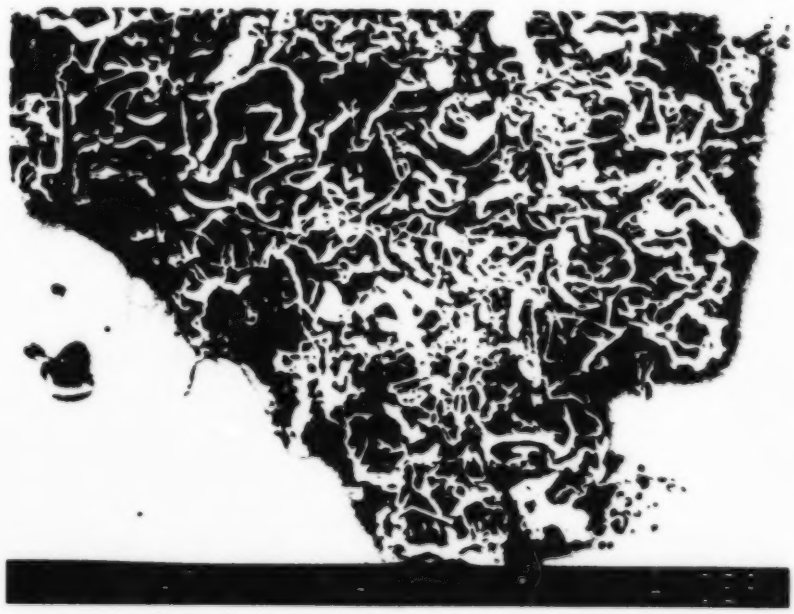

FIGURE 2.24 AN ELECTRON MICROGRAPH OF THE PARTICLES FROM SAMPLE #6 SHOWN IN FIGURE 2.23 (MAGNIFICATION 450X)

FIGURE 2.25 A METALLIC PARTICLE FROM SAMPLE #6 (MAGNIFICATION 400X)

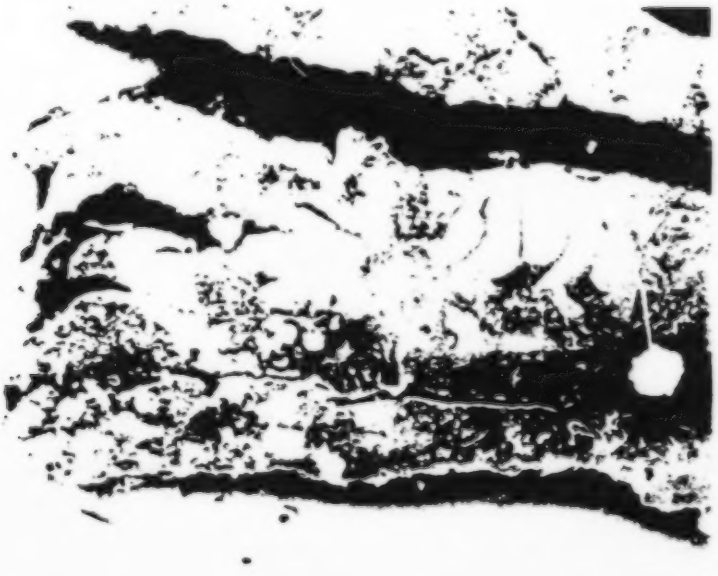

FIGURE 2.26 AN ELECTRON MICROGRAPH OF THE PARTICLE FROM SAMPLE #6 SHOWN IN FIGURE 2.25 (MAGNIFICATION 450X)

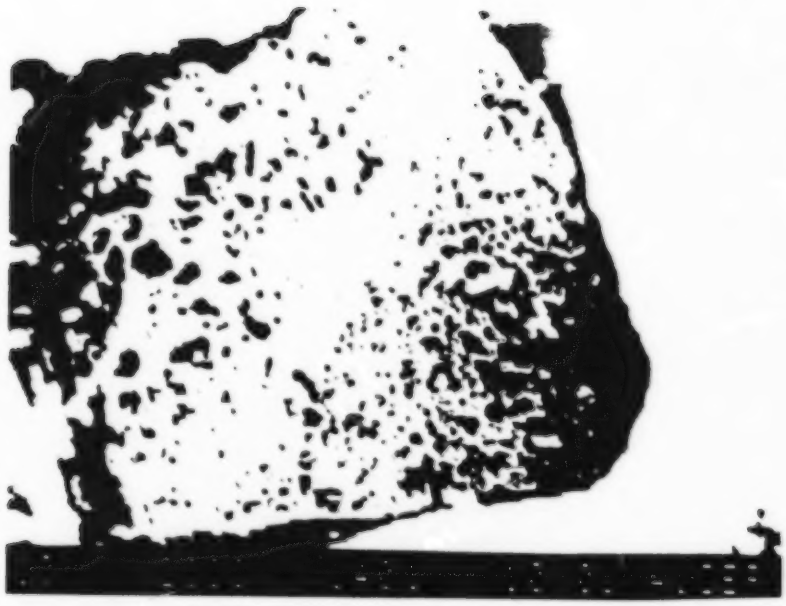

FIGURE 2.27 AN ELECTRON MICROGRAPH OF A MAGNETITE PARTICLE FROM SAMPLE #7 (MAGNIFICATION 2000X)

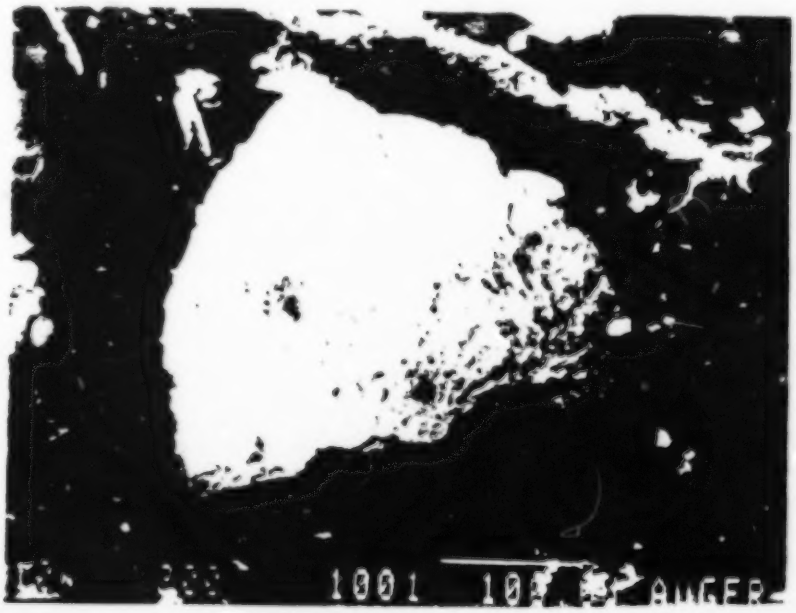

FIGURE 2.28 AN ELECTRON MICROGRAPH OF A ZIRCONIUM OXIDE PARTICLE FROM SAMPLE #7 (MAGNIFICATION 200X)